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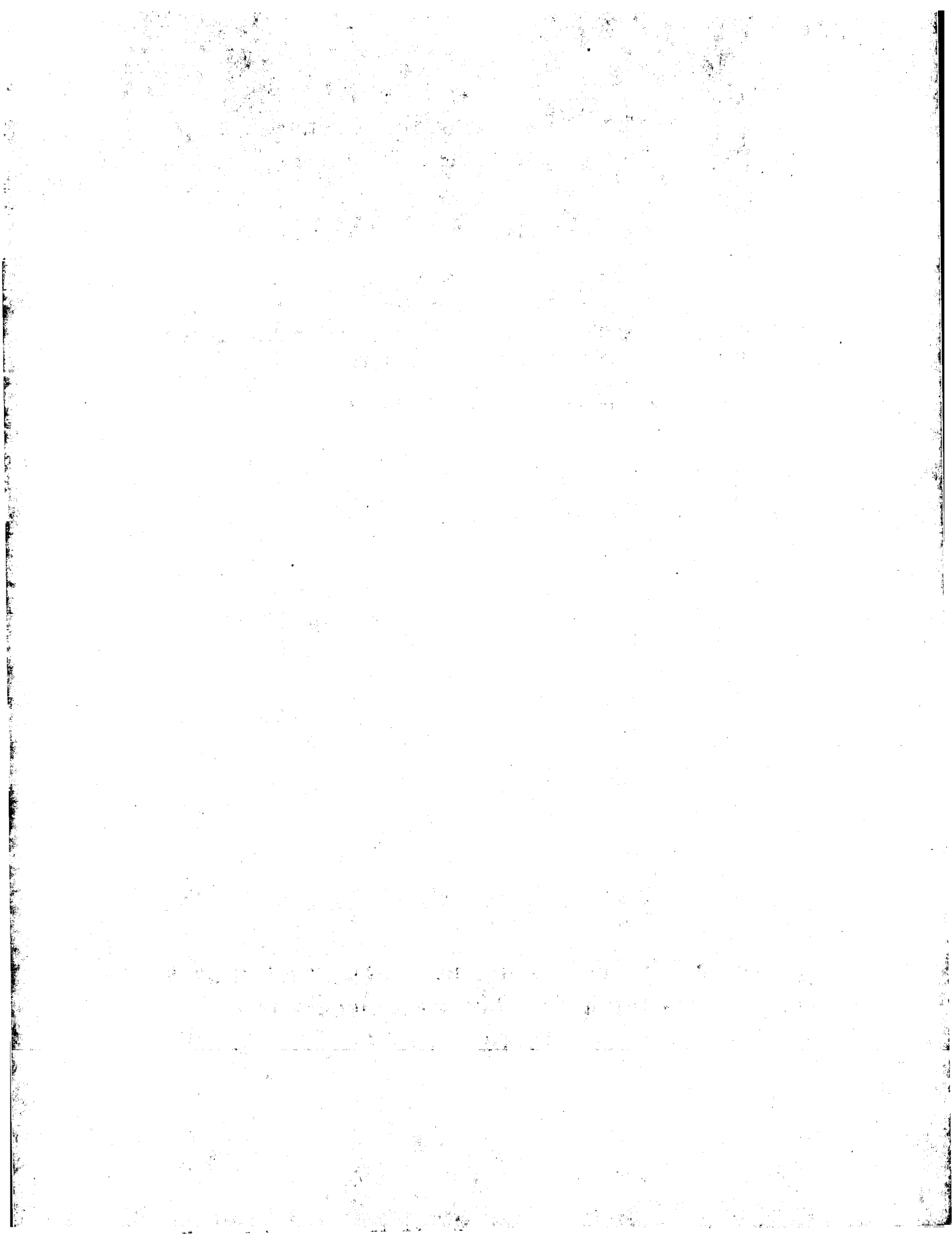
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(54) Protected optical brighteners.

(57) Protected additives for use in cleaning compositions such as liquid laundry detergents comprises an optical brightener, bleach, photoactive bleach, perfume, blueing agent or dye dispersed in, or coated with, a hydrophobic substance such as silicone oil or a hydrocarbon, which is insoluble in concentrated liquid detergent but which is disrupted under normal cleaning conditions.

EP 0 273 775 A2

Description

PROTECTED OPTICAL BRIGHTENERS

The present invention relates to protected detergent additives, including optical brighteners, bleaches and other fabric whitening agents, perfumes and dyes, which are suitable for use in liquid laundry detergents.

Optical brighteners, blueing agents, peroxygenated and chlorinated bleaches, and photoactivated bleaches have long been known as ingredients of detergent formulations, and are referred to collectively herein as fabric whitening agents. Optical brightening agents are fluorescent dyes which increase the brightness of laundered fabrics by absorbing ultraviolet light and reradiating the energy as visible light. Blueing agents are blue dyes which counteract the tendency of fabrics to yellow after repeated washing and chemical bleaches react chemically with stains, e.g. oxidising them to colourless products.

For the purposes of this specification the acronym O.B.A. will be used for convenience to include not only the conventional fluorescent optical brightening agents to which it properly applies, but also any other minor additive to a liquid detergent which is capable, on application to fabric, of altering the appearance thereof relative to the clean untreated fabric, and in particular to include chemical bleaches, photoactivated bleaches, blueing agents, perfumes and dyes.

Liquid laundry detergents are increasingly replacing the more traditional powders in the marketplace, due to certain advantages in handling and use. In particular liquid detergents are popular because they can be used for "prespotting" - that is application of the undiluted liquid directly to a localised stain prior to laundering.

It has been found that on certain kinds of fabric, especially linen, and to a lesser extent cotton, the O.B.A.s in liquid laundry detergents can change the appearance of a prespotted area relative to that of the surrounding fabric, after both have been washed clean. Hitherto the only effective solution to this problem has been to market a special formulation for prespotting which does not contain any of the more effective O.B.A.s and which is therefore unsuitable for use as a main wash detergent.

As a result one of the major advantages of liquid laundry detergents over powders is not reliably available in formulations designed for main wash use. A single formulation capable of use for both prespotting and main wash is a major commercial objective.

Other difficulties, which have been observed when O.B.A.s are added to liquid detergents, include the adverse effect which certain O.B.A.s may have on the stability or viscosity of many structured liquid detergent formulations, the mutual chemical or physical incompatibility of certain O.B.A.s when used in conjunction with one another in a liquid detergent, and the poor chemical stability of some O.B.A.s in the presence of liquid detergent.

Our invention provides a novel composition which offers a means of incorporating O.B.A.s into liquid detergents and which substantially ameliorates or avoids many of the foregoing difficulties. In particular it helps reduce or prevent any localised discolouration due to excessive adsorption of O.B.A. from the undiluted heavy duty liquid on prespotting, and any incompatibility between the O.B.A. and the liquid detergent or other O.B.A.s present therein, but enables the O.B.A. to perform effectively when applied to the main wash.

We have now discovered that when O.B.A.s are suspended, dispersed or encapsulated in a hydrophobic substance which is liquid or friable at wash temperature, but which does not dissolve in a concentrated liquid detergent, and the resulting protected system is dispersed as discrete droplets or particles in the detergent, the detergent may be applied, undiluted, to localised areas of the fabric with substantially reduced risk of local discolouration. We have further discovered that when added to a wash liquor and agitated in the presence of clothes, the detergent exhibits effective brightening characteristics.

According to one aspect our invention therefore provides a protected O.B.A. system suitable for use in a liquid cleaning composition, said system comprising at least one O.B.A. dispersed in or coated with a hydrophobic protective substance, which is insoluble in concentrated liquid detergent but dispersible therein as particles or droplets, and which is sufficiently fluid or friable at wash temperature to be disrupted under cleaning conditions.

According to a second embodiment our invention provides a protected O.B.A. system for use in a liquid cleaning composition consisting essentially of granules comprising at least one O.B.A. encapsulated within a hydrophobic protective substance which is not soluble in the liquid cleaning composition and which is fluid or friable at normal wash temperatures.

According to a third embodiment our invention provides a protected O.B.A. system for use in liquid detergent compositions consisting essentially of a dispersion of O.B.A. in a hydrophobic liquid which is insoluble in liquid detergent.

According to a fourth embodiment our invention provides a method of protecting O.B.A. which comprises dispersing an O.B.A. in a hydrophobic protective substance which is insoluble in concentrated liquid detergent at room temperature, and fluid or friable at 60°C.

According to a fifth embodiment our invention provides a liquid cleaning composition having dispersed therein particles or droplets of a protected O.B.A. system of our invention as hereinbefore described.

References herein to solubility in a medium refer to both dissolution in an aqueous or other continuous solvent phase of the medium and solubilisation in micelles or any other discontinuous surfactant phase dispersed in the medium.

The hydrophobic material is preferably a hydrophobic liquid polymer. For example the polymer may be an

organo polysiloxane oil, e.g. a poly di(alkyl)siloxane, wherein the alkyl group has preferably from 1 to 4 carbon atoms, especially a poly di(methyl) siloxane. Especially preferred are hydrophobic liquids which have been stabilised by suspending therein hydrophobic solid particles. Examples include the silicone compositions which have been proposed for use as antifoam in liquid detergents which comprise hydrophobic silicone oil and hydrophobic silica, e.g. a finely divided silica with a silicone at least partly bonded to the surface of the silica particles. For example a hydroxy functional organosiloxane may be condensed with the hydroxy groups of the silica surface. Examples of such compositions include those sold under the Registered Trade Marks "WACKER" Antifoam S132, "BEVALOID" 4237, "UNION CARBIDE" Y1206, or DIAMOND SHAM-ROCK'S "NOPCO" 8315. The silicone antifoam may be diluted with an unmodified silicone oil such as a poly dimethyl siloxane. Furthermore the viscosity of the silicone may be increased by addition of finely divided silica, e.g. fumed silica such as Degussa's "AEROSIL" 200 (RTM).

Alternatively the hydrophobic material may be a high molecular weight hydrocarbon, e.g. petroleum bright stock or a so-called petroleum jelly, a high molecular weight alcohol, e.g. more than 28 carbon atoms or a high molecular weight fluorocarbon or a hydrophobic phosphate ester such as a mono- and/or di- fatty alkyl phosphate ester or a salt thereof, especially a sodium or calcium salt or a triaryl or trialkyl phosphate. Hydrophobic fluid materials may be further stabilised by inclusion of hydrophobic solid particles, e.g. those formed by condensing silica with silicone as described above or with a fatty alcohol. According to one embodiment the hydrophobic material may be a solid or waxy material at ambient temperature, which has a softening or preferably melting point below normal wash temperature, e.g. below 60°C, preferably below 50°C, more usually 40°C, often below 30°C. Such solid materials provide products which are particularly suitable for use in powder as well as liquid detergents. Typically we prefer that our hydrophobic material has a viscosity greater than 0.05 Pascal seconds at normal storage temperature (e.g. room temperature) preferably greater than 0.2, more preferably greater than 0.5 and most preferably greater than 0.8 Pascal seconds. In particular we prefer that the viscosity should be greater than 1 Pascal second e.g. greater than 2 Pascal seconds, especially greater than 10 Pascal seconds. We prefer that the viscosity should be less than 200 Pascal seconds, most preferably less than 100 Pascal seconds, e.g. less than 60 Pascal seconds and especially less than 40 Pascal seconds, at the temperature of use. Fluid materials having a viscosity between 1 and 50 Pascal seconds at ambient temperature are especially suitable.

Unless stated to the contrary, all references herein to viscosities are as measured at 24 sec⁻¹ shear and at 25°C.

The O.B.A. may be any fluorescent dye capable of increasing the proportion of light reflected from fabric at visible wavelengths such as suphonated aromatic dyes including any of those hitherto recommended or proposed for use in detergents.

Typical examples of O.B.A.s which may be used in the present invention include: ethoxylated 1, 2-(benzimidazolyl) ethylene; 2-styrylnaphth[1,2d]oxazole; 1,2-bis(5'-methyl-2-benzoxazolyl) ethylene; disodium-4,4'-bis(6-methylethanolamine-3-anilino-1,3,5-triazin-2''-yl)-2,2'-stilbene sulphonate; N-(2-hydroxyethyl-4,4'-bis (benzimidazolyl)stilbene; tetrasodium 4,4'-bis [4''-bis(2''-hydroxymethyl)-amino-6''(3''-sulphophenyl) amino-1'', 3'', 5''-triazin-2''-yl amino]-2,2'-stilbenedisulphonate; disodium-4-(6''-sulphonaphtho[1',2'-d]triazol-2-yl)-2-stilbenesulphonate; disodium 4,4'-bis [4''-(2'''-hydroxyethoxy)-6''-amino-1'',3'',5''-triazin-2''-yl amino] 2,2'-stilbenedisulphonate; 4-methyl-7-dimethyl aminocoumarin; and alkoxyated 4,4'-bis-(benzimidazolyl) stilbene.

Other O.B.A.s which may be used according to our invention include blueing agents, dyes, colourants, perfumes, peroxy bleaches and photoactive bleaches. Examples include sodium peroxide or, preferably, peroxy carboxylic acids such as peroxy acetic, peroxy benzoic and peroxy fatty acids and especially C₆₋₂₀ alkyl di peroxy dioic acids (e.g. diperoxy dodecane dioic acid). Chlorinated bleaches, such as sodium hypochlorite and photoactivated bleaches may also be protected according to the invention as may perfumes.

The protected system may additionally comprise stabilisers, activators or synergists for the O.B.A. For example peroxy bleaches may be stabilised by the presence of phosphonate salts such as dimerised acetodiphosphonate salts or amino tris (methylenephosphonate), ethylenediamine tetrakis (methylenephosphonate) or diethylenetriamine pentakis (methylenephosphonate).

The O.B.A. may be present in the hydrophobic material in the form of dispersed droplets of a solution of O.B.A. in a solvent, e.g. in water or a lower, preferably water miscible, mono-, di- or polyhydric alcohol such as propylene glycol, where the O.B.A. is water-soluble.

Alternatively the O.B.A. may be present in the form of suspended solid particles.

The O.B.A. may also be present in a water soluble granule or marume. Thus a soluble crystalline carbohydrate such as sucrose or a salt such as sodium chloride, sodium carbonate or sodium sulphate may be granulated or marumerised with the O.B.A. and the product dispersed in, or coated with, silicone or a hydrocarbon, such as petroleum jelly or other hydrophobic agent.

The O.B.A. may be incorporated in an inert oil by dispersion by simple stirring. Where the hydrophobic material is solid at room temperature it may first be melted before dispersing the O.B.A. and subsequently cooled to room temperature. Optionally the dispersion may be spray cooled to provide a particulate product.

The proportion of O.B.A. in a liquid protected system may be determined by the desired viscosity of the system, where it is desired to handle or store the latter as a liquid. Higher proportions tend to provide higher viscosities, but are less prone to sedimentation of the dispersed O.B.A. However, we do not exclude the use of sedimenting systems provided that the O.B.A. can be easily redispersed by stirring before the system is added

to the detergent composition.

Preferably the particle size and proportion of the O.B.A. in liquid protected systems are chosen to provide an overall viscosity of the protected system greater than 0.1 Pascal seconds, typically greater than 0.5 Pascal seconds especially greater than 1 Pascal second more preferably greater than 2 Pascal seconds, e.g. greater than 3 Pascal seconds and optionally greater than 10 Pascal seconds, under the conditions of storage and less than 200 Pascal seconds, more preferably less than 100 Pascal seconds, e.g. less than 70 Pascal seconds under the conditions of use. Systems having a viscosity in the range of 2 to 60 Pascal seconds at ambient temperature are generally preferred.

Where O.B.A. is incorporated in the system as a solution, the solution preferably contains 1 to 90% by weight of O.B.A., e.g. 2 to 80%, typically 5 to 60%, and its dispersion in the oil typically contains 1-80, more usually 5-70, preferably 10-60, more preferably 15-50, e.g. 20-40 or 30-50% by weight of O.B.A. solution, the percentages being expressed by weight of the total protected system. Suspensions of solid O.B.A. in the protective material typically contain 1 to 90, more usually 5 to 80, preferably 20-60, e.g. 30-50 or 20-30% by weight of solid, based on the total weight of suspension.

The proportion of O.B.A. in the protected system may depend on whether the hydrophobic substance is required to perform any useful function in its own right, e.g. as antifoam. Where a low foaming composition is required the O.B.A. and antifoam may conveniently be in the same relative proportions as those which are required in the final composition. Alternatively a more concentrated suspension of O.B.A. may be prepared and diluted with more antifoam prior to use, or added to the composition simultaneously with or separately from the additional antifoam.

Where the hydrophobic material is not required to perform a useful function other than protecting O.B.A., the concentration of the latter may be the maximum which is consistent with a manageable product.

The particle size of the dispersed O.B.A. in the protected system can vary within wide limits. Typically the dispersed O.B.A. may have a particle size in the range 1 μ to 2mm, preferably 5 μ to 1mm, e.g. 10 μ -700 μ .

The protected system is generally readily dispersed in the liquid detergent by simple stirring. The system may be dispersed as particles or droplets of from 2 μ to 2.5mm diameter, more usually 5 μ -500 μ , preferably 10 μ -100 μ , where a dispersed solution is used as the protected system. Where the O.B.A. is present as a coated granulate, the preferred particle size of the system in the liquid detergent is 500 μ to 1mm.

Dispersants and emulsifiers may be used as required but are not usually preferred.

Preferably the composition is added to a liquid detergent which comprises an aqueous phase, surfactant, sufficient electrolyte dissolved in the aqueous phase to form with the surfactant, a structure capable of supporting suspended particles, and a protected O.B.A. system of our invention, suspended in the detergent composition.

Preferably the composition contains an effective amount of a detergent builder. Suitable builders include condensed phosphates, especially sodium tripolyphosphate or, less preferably, potassium pyrophosphate or sodium tetrakisphosphate, sodium carbonate, sodium silicate, sodium orthophosphate, sodium citrate, sodium nitrilotriacetate, a phosphonate such as sodium ethylenediamine tetramethylene phosphonate, sodium aceto diphosphonate or sodium aminotris (methylene phosphonate), sodium ethylenediamine tetracetate or a zeolite. Other less preferred builders include potassium or lithium analogues of the above sodium salts.

The proportion of builder is typically from about 5% to about 40% by weight of the liquid detergent composition, usually 10% to 35%, preferably 15%-30%, more preferably 18% to 28%, most preferably 20 to 27%. Mixtures of two or more builders are often employed, e.g. sodium tripolyphosphate with sodium silicate and/or sodium carbonate, or with zeolite; or sodium nitrilotriacetate with sodium citrate.

Preferably the builder is at least partly present as solid particles suspended in the composition.

Particularly preferred are liquid detergent compositions according to the aforesaid GB 2,123,846 or GB 2,153,380.

The invention is also applicable to the preparation of unbuilt surfactant compositions or compositions in which all the builder is present in solution.

The surfactant may be an anionic, nonionic, cationic, amphoteric, zwitterionic and/or semi polar surfactant which may typically be present in concentrations of from 2 to 35% by weight of the composition, preferably 5 to 30%, more usually 7 to 25%, e.g. 10 to 20%.

Usually the composition contains an alkyl benzene sulphonate together with one or more other surfactants such as an alkyl polyoxyalkylene sulphate and/or a non-ionic surfactant. The latter may typically be an alkanolamide or a polyoxyalkylated alcohol.

Other anionic surfactants include alkyl sulphate, alkane sulphonates, olefin sulphonate, fatty ester sulphonates, soaps, alkyl sulphosuccinates, alkyl sulphosuccinamates, taurides, isethionates and polyoxyalkylene derivatives of the aforesaid categories of anionic surfactant. In every case the surfactant for use herein has an alkyl group with an average of from 8 to 22, preferably 10 to 20, e.g. 12 to 18 carbon atoms. Alkyl groups are preferably primary and straight chain, however we do not exclude branched chain or secondary alkyl groups. In the case of alcohol based non-ionics the branched chain are sometimes preferred.

The surfactant may be wholly or predominantly non-ionic, e.g. a polyoxyalkylated alcohol alone or in admixture with a polyoxyalkylene glycol. Other non-ionic surfactants which may be used include polyoxyalkylated derivatives of carboxylic acids, glycerol, sorbitan, alkylphenols, alkylolamides or amine oxides.

All references herein to polyoxyalkylene groups are preferably to polyoxyethylene groups, or less preferably

to polyoxypropylene or mixed oxyethylene oxypropylene copolymeric or block copolymeric groups or to such groups with one or more glyceryl groups. Preferably the polyoxyalkylene groups have from 1 to 30, more usually 2 to 20, e.g. 5 to 15, alkyleneoxy units.

Cationic surfactants for use according to our invention include quaternised alkyl amines, amido amines and imidazolines. Amphoteric surfactants include betaines and sulphobetaines.

In general any surfactant referred to in GB 1,123,846, or in "Surface Active Agents and Detergents" by Schwartz, Perry and Berch, may be used.

Preferably the pH of the liquid detergent composition is alkaline, e.g. about 7.5, especially 7.5 to 12 typically 8 to 11, e.g. 9 to 10.5.

Preferably the liquid detergent composition contains dissolved electrolyte. This may comprise a dissolved portion of the builder and/or any other salt, inorganic or organic, which is not itself a surfactant and which salts out the surfactants present from solution (including micellar solution). Examples include sodium chloride, sodium nitrate, sodium bromide, sodium iodide, sodium borate, sodium formate, or sodium acetate, or corresponding potassium salts. Preferably, however, the electrolyte is a salt which is required to perform a useful function in the wash liquor.

The electrolyte is preferably sufficient to form a spherulitic or lamellar surfactant structure interspersed with an aqueous electrolyte solution.

The electrolyte may comprise sodium sulphate in minor concentrations, but electrolyte mixtures containing concentrations of sodium sulphate of about 3% or over, based on the total weight of the detergent composition, are preferably not used because they may give rise to undesirably large crystals of sodium sulphate of more than 1mm in length, e.g. up to 5cm, or even longer.

The detergent composition may contain any of the usual minor ingredients such as soil suspending agents (e.g. carboxymethyl cellulose), enzymes, perfumes and bentonite clays.

Particularly preferred liquid detergents are those containing long chain, e.g. C₁₀₋₁₄ linear alkyl benzene sulphonates in an amount of 5-12%, long chain alkyl ether sulphonates, e.g. with 1-5 ethyleneoxy units in amount of 0-3%, fatty acid alkanolamides, e.g. lethanolamides in amount of 1-5%, mixtures of mono and di long chain alkyl phosphates in amount of 0-3%, e.g. 0.1-1%, sodium tripolyphosphate (preferably pre-hydrated with from 0.5 to 5% by weight of water) in an amount of 14-30%, e.g. 14-18% or 20-30% and optionally sodium carbonate in an amount of up to 10%, e.g. 5-10%, with the total of sodium tripolyphosphate and carbonate of 20-30%, antiredeposition agents such as sodium carboxymethyl cellulose in amount of 0.05-0.5%, enzyme systems in an amount of 0.05-0.5%, chelating agents, e.g. amino phosphonates such as methylene phosphonates of di and polyamines especially sodium ethylenediamine tetra[methylene phosphonate] or diethylene triamine hexa[methylene phosphonate] optionally present in amount of 0.1-1%, together with conventional additives such as perfume, the remainder being water, the percentages being by weight of the total liquid detergent. The liquid detergent may have a pH of 6 to 13, preferably 7 to 12, more usually 8 to 11, e.g. 9 to 10.5.

The compositions of the invention may typically contain 0.01 to 10%, e.g. 0.05-0.5% by weight of the protected O.B.A. system.

A particular advantage of the present invention is that it assists in the formulation of stable detergents by inhibiting possible interactions between the O.B.A. and any other component of the detergent which may be chemically incompatible therewith. Thus the hydrophobic substance may protect peroxide bleaches from hydrolysis in an alkaline aqueous liquid detergent, or prevent interaction between bleaches and dyes in the composition. The compositions of our invention may advantageously be added to solid, powder detergents as well as to liquid detergents, in order to inhibit interactions between the O.B.A.'s and other components of the powder cleaning compositions. Powder cleaning compositions containing protected O.B.A.'s as hereinbefore described constitute a further aspect of this invention.

For instance O.B.A. dispersed in silicone antifoam, polyvinyl alcohol or viscous hydrocarbon may be incorporated into a powder laundry detergent. Conventionally such powders may contain surfactant (usually in total amounts of from 5 to 30% by wt.), builder, a solid filler and optionally a bleach. Usually the surfactant comprises a sodium alkyl (preferably C₁₂₋₁₄ linear) benzene sulphonate in amounts of from 2 to 20%, preferably 5 to 15%, by weight of the total composition and optionally a sodium alkyl (e.g. C₁₂₋₁₈) polyoxyethylene (e.g. 2 to 10% mole) sulphate and/or a non-ionic surfactant such as an alkanolamide, e.g. coconut, mono- or di- ethanolamide and/or a polyethoxylated fatty alcohol.

The builder is typically sodium tripolyphosphate although zeolites, sodium carbonate, sodium silicates, sodium citrate, sodium nitrilotriacetate and mixtures thereof may be present as well as or in place of sodium tripolyphosphate. The total amount of builder is usually between 10 and 40% by weight of the total powder, e.g. 20 to 30%.

The filler is typically sodium sulphate which may typically be present in a proportion of from 0 to 60% usually 20 to 50% of the total composition in order to ensure a free flowing powder.

The powder preferably contains at least two protected O.B.A. systems including a fluorescent brightening agent and a bleach.

The bleach is normally a peroxy compound especially a perborate, percarbonate or peroxy-carboxylic acid.

The powder also usually contains the usual minor ingredients such as soil suspending agent (typically sodium carboxymethyl cellulose), enzymes and perfume and optionally colouring.

Protected O.B.A. systems according to our invention may be added to machine dishwashing powders,

scouring creams and other hard surface cleaners, carpet shampoos, degreasing compositions, oven cleaners, dishwashing liquids, soap powders, laundry pre-soak compositions and other cleaning preparations.

Dishwashing powders according to our invention may typically comprise a substantial proportion, e.g. 20 to 60%, preferably 30 to 50%, of an alkali such as a sodium carbonate and a minor proportion, e.g. 1 to 5%, of surfactant preferably a non-ionic surfactant such as an alkoxyated alcohol, together, optionally but preferably, with a builder such as sodium tripolyphosphate in proportions of up to about 45% by weight of the composition, e.g. 20 to 35%, an alkaline silicate such as sodium metasilicate and an alkaline buffer such as borax. The protected O.B.A. preferably comprises a bleach such as chlorinated trisodium phosphate in a proportion of from 0.1 to 5%, preferably 0.5 to 3%, e.g. 1 to 2%.

Liquid dishwashing compositions of our invention typically comprise highly soluble builders such as potassium pyrophosphate, and/or potassium silicate in a total concentration of 10 to 30% by weight, surfactants, preferably non-ionic in concentrations of 0.2 to 5% by weight and hydrotropes such as sodium xylene sulphonate, sodium toluene sulphonate or sodium benzene sulphonate in concentrations of 1 to 10% by weight.

Hard surface cleaners of our invention may typically comprise 1 to 10%, surfactant, typically non-ionic or anionic/nonionic mixtures, 1 to 10% hydrotrope and 2 to 10% soluble builder such as potassium pyrophosphate. Hard surface cleaners may also optionally comprise abrasives such as silica, or calcium carbonate as arragonite or calcite suspended in a structural liquid.

Carpet shampoos according to our invention may according to our invention comprise relatively high concentrations, e.g. 5 to 20% by weight, of high foaming surfactants such as mixtures of anionic surfactants (e.g. alkyl sulphates) with foaming agents (e.g. alkanolamides).

Oven cleaners according to our invention may be of the caustic type comprising, e.g. 4 to 12% of alkalis such as sodium hydroxide, and typically a high foaming anionic surfactant such as a sodium alkyl ether sulphate, or else of the solvent based type containing e.g. 10 to 30% of a water miscible organic solvent such as a lower mon- di- or polyhydric alcohol or other alcohol, e.g. propylene glycol, and typically a non ionic surfactant, together preferably with a builder such as sodium tripolyphosphate.

Any difficulties in dispersing the protected O.B.A. system in any of the foregoing liquid formulations is generally avoided by addition of small amounts of conventional dispersants or suspending agents such as soluble gums or polyelectrolytes.

Normal wash conditions for laundry detergents involve temperatures of from 50°C to 60°C and a wash liquor containing about 2 to 15 gm per litre of detergent composition under vigorous agitation. Some detergents, however, are formulated and recommended for use at cool or intermediate wash temperatures (20 to 30° or 30 to 40°C respectively), either for sensitive fabrics or energy saving.

Without prejudice to the generality of the foregoing disclosure a protected O.B.A. system for use in a specific liquid cleaning composition shall be deemed insoluble therein for the purposes of this specification, if it is not appreciably soluble at 20°C. Other protected O.B.A. systems shall be deemed insoluble in liquid detergent if they are not appreciably soluble in the detergent composition of Example 1 at 20°C.

Protected O.B.A. systems shall be deemed fluid or friable under wash conditions if they release O.B.A. into contact with any fabric present when agitated in a washing machine in a wash liquor containing the relevant cleaning composition at a total solids concentration of 0.5% and at 60°C.

Our invention is illustrated by the following examples.

Example 1

The O.B.A., a 4,4'-distyryl biphenyl compound sold by Ciba Geigy under the registered trade mark "TINOPAL" CBS-X, was ground in a ball mill with a polymethyl siloxane oil containing fumed silica currently sold by Wacker under the trade designation S132 in a proportion of one part O.B.A. to four of silicone oil.

A liquid detergent formulation was prepared having the following composition by weight.

Sodium linear C ₁₂₋₁₄ alkyl benzene sulphonate	6%
Sodium linear C ₁₂₋₁₈ alkyl 3-mole ethoxy sulphate	2%
Coconut diethanolamide	1.5%
Sodium tripolyphosphate	25%
Sodium carboxymethyl cellulose	0.1%
Sodium salt of a mixed mono/bis C ₁₆₋₁₈ alkyl ethylenediamine tetrakis (methylene phosphonate) ester sold by Albright & Wilson Limited under the registered trade mark "BRIQUEST" 543-S	0.5%
Perfume	0.3%

The liquid was divided into three portions. To one was added 0.05% by weight of the unprotected O.B.A., to the second one was added 0.25% by weight of the O.B.A./silicone oil and the third was retained as a control. Each of the first two samples was thoroughly mixed with the added O.B.A., and 2gm drops of the three detergents samples were applied to separate areas of a blue-dyed linen cloth and rubbed gently with a finger to form spots of equal area. After 1 minute the fabric was laundered in a washing machine without further addition of detergent. After rinsing and drying the cloth was inspected under U.V. light and the excess absorption of O.B.A. compared to the untreated cloth measured by visually estimating the intensity of whitening.

The result in order of increasing whiteness was:

Control sample -1
 Untreated cloth 0
 Example of invention 2
 unprotected O.B.A. 5

5

When added directly to a washing machine as a main wash detergent, the sample containing silicone protected O.B.A. performs similarly to the sample containing the unprotected O.B.A.

Examples 2-4

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10% by weight of a mixture of sodium sulphate and diperoxidodecylidicarboxylic acid (DPDDA) in a weight ratio of 88:1 was suspended in the liquid detergent formulation of Example 1 to provide comparative Example B. The second portion of the same mixture was first mixed with an equal weight of silicone oil (Wacker S132) to provide Example 2 and a third portion was first mixed with 80%, based on the weight of solid mixture, of "BEVALOID" 4237 silicone oil to provide Example 3.

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0% stain removal on EMPA 114 test cloth by the three detergent formulations was compared with the base detergent (Comparative Example B) after 3, 7, 11 and 19 days as follows:

No. of days	0	3	7	11	19
Comparative Example A	80	82	77	77	78
Comparative Example B	110	88	85	86	87
Example 2	109	93	90	88	88
Example 3	111	90	84	85	87

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High sulphate compositions such as comparative Example B notoriously give rise to the formation of large needle-shaped crystals of sodium sulphate on standing.

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Moreover no such crystallisation was observed in the case of Example 2 and 3.

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Claims

1. A protected system suitable for use in cleaning compositions, comprising at least one compound selected from optical brightening agents, bleaches, photoactive bleaches, blueing agents, perfumes and dyes dispersed in, or coated with, a hydrophobic protective substance which is insoluble in concentrated liquid detergent but dispersible therein as particles or droplets, and which is sufficiently fluid or friable at wash temperature to be disrupted under cleaning conditions.

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2. A protected system according to claim 1, comprising granules, wherein said compound is encapsulated within said hydrophobic protective substance.

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3. A system according to claim 1, comprising a dispersion of said compound in a hydrophobic substance which is insoluble in liquid detergent at room temperature and which is liquid at 60°C.

4. A system according to claim 1, wherein said hydrophobic protective substance is a polymer which is liquid at room temperatures.

5. A system according to claim 4, wherein said hydrophobic protective substance is an organopolysiloxane oil.

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6. A system according to any of claims 1 to 3, wherein said hydrophobic protective substance is a hydrocarbon.

7. A system according to any foregoing claim, wherein said compound is a fluorescent dye.

8. A system according to any of claims 1 to 6, wherein said compound is an oxidising bleach.

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9. A system according to any of claims 1 to 6, wherein said compound is a photoactive bleach.

10. A system according to claim 8, wherein said oxidising bleach is a peroxy carboxylic acid.

11. A system according to any foregoing claim, comprising droplets of a solution of said compound in a solvent dispersed in a liquid hydrophobic substance.

12. A system according to any of claims 1 to 10, comprising a water-soluble granule or marume dispersed in, or coated with, a silicone or hydrocarbon.

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13. A liquid detergent composition having dispersed therein a protected system according to any foregoing claim.

14. A detergent powder comprising a protected system according to any of claims 1 to 12.

15. A detergent powder containing a protected system according to claim 12.

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16. A detergent composition according to any of claims 13 to 15, containing two or more different protected systems.

17. A composition according to claim 16 containing a protected fluorescent dye and a protected bleach.

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⑫ **EUROPEAN PATENT APPLICATION**

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㉗ **Protected optical brighteners.**

㉘ Protected additives for use in cleaning compositions such as liquid laundry detergents comprises an optical brightener, bleach, photoactive bleach, perfume, blueing agent or dye dispersed in, or coated with, a hydrophobic substance such as silicone oil or a hydrocarbon, which is insoluble in concentrated liquid detergent but which is disrupted under normal cleaning conditions.

EP 0 273 775 A3



EP 87 31 1536

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	EP-A-0 206 718 (CLOROX) * Page 3, lines 8-17; page 9, lines 5-11; examples; claims *	1	C 11 D 3/42 C 11 D 3/395 C 11 D 3/40 C 11 D 3/50
X	US-A-4 708 816 (D.M. CHANG et al.) * Claims *	1-2	
A	US-A-4 090 973 (E.J. MAGUIRE, Jr. et al.) * Claims *	1	
P, X	EP-A-0 238 216 (ALBRIGHT & WILSON) * Claims *	1-17	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 11 D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-02-1989	Examiner GOLLER P.
CATEGORY OF CITED DOCUMENTS			
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			